A $\gamma$-ray and dual redox-responsive supramolecular polymer constructed by a selenium containing pillar[5]arene dimer and a neutral guest

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Copillar[5]arene,$^{51}$ Na$_2$Se$_2$$^{52}$ and G$^{53}$ were prepared according to a published procedure. $^1$H NMR, $^{77}$Se NMR and $^{13}$C NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or Bruker Avance DMX 500 or Bruker Avance DMX 600 using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 Tesla FTMS. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298K in water. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument.


Copillar[5]arene was synthesized according to previous literature. NaSeSeNa (1.5 mmol, 3ml) solution was added with magnetic stirring to copillar[5]arene (0.73 g, 0.9 mmol) THF solution with N\textsubscript{2} protection. The mixture was stirred for 24 h at 50 °C. Then the solvent was removed and the combined mixture was further purified by silica gel column chromatography eluting with 1:1 dichloromethane: petroleum ether. The evaporation of the solvent gave the yellow powder (0.71 g, 90%). The \textsuperscript{1}H NMR spectrum of 1 is shown in Fig. S1. \textsuperscript{1}H NMR (400 MHz, chloroform-\textit{d}, 293 K) δ (ppm): 6.8–6.72 (m, 10 H), 3.8–3.77 (m, 12 H), 3.66–3.58 (m, 27 H), 2.87 (s, 2H), 1.78 (s, 4H). The \textsuperscript{77}Se NMR spectrum of 1 is shown in Fig. S2. \textsuperscript{77}Se NMR (600 MHz, chloroform-\textit{d}, 293 K) δ (ppm): 304.71. The \textsuperscript{13}C NMR spectrum of 1 is shown in Fig. S3. \textsuperscript{13}C NMR (100 MHz, chloroform-\textit{d}, 293 K) δ (ppm): 150.85, 150.78, 149.76, 128.26, 114.78, 114.14, 67.38, 55.85, 55.79, 55.69, 53.38, 31.54, 29.68, 22.43, 14.13. LRESIMS is shown in Fig. S4: \textit{m/z} 1760.1 [1 + \textit{NH}_4]^+\textsuperscript{+}. HRESIMS is shown in Fig. S5: \textit{m/z} calcd for [1 + \textit{NH}_4]^+\textsuperscript{+} C\textsubscript{96}H\textsubscript{114}O\textsubscript{20}Se\textsubscript{2}N\textsubscript{4}, 1760.6330; found 1760.5959; error 21 ppm.
**Fig. S1** $^1$H NMR spectrum (400 MHz, chloroform-$d$, 293K) of pillar[5]arene dimer 1.

**Fig. S2** $^{77}$Se NMR spectrum (600 MHz, chloroform-$d$, 293K) of pillar[5]arene dimer 1.
Fig. S3 ¹³C NMR spectrum (100 MHz, chloroform-"d, 293K) of pillar[5]arene dimer 1.

Fig. S4 Electrospray ionization mass spectra of pillar[5]arene dimer 1. Assignment of the main peak: m/z 1760.1 [1 + NH₄]⁺.
Fig. S5 High resolution electrospray ionization mass spectra of pillar[5]arene dimer 1.

3. Synthesis of neutral guest 2

Scheme S2. Synthetic route to 2.

5-Azidepentanenitrile 2a was prepared according to previous literature. Sodium azide (0.95 g, 15 mmol) was added to a solution of 5-bromopentanenitrile (2.0 g, 12 mmol) in dry N, N-dimethylformamide (30 mL). The reaction mixture was stirred at 80 °C for 10 h. After completion, the cooled reaction mixture was added to diethyl ether (100 mL). The solution was washed with H₂O (2 × 100 mL) and brine (2 × 50 mL), and dried over anhydrous Na₂SO₄. The organic layer was removed under vacuum to give 2a (1.8 g, 92 %) as an oil. ¹H NMR spectrum of 2a is shown in Fig. S6. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 1.75 (t, J = 4 Hz, 4H), 2.41 (t, J = 12 Hz, 2H), 3.37 (t, J = 12 Hz, 2H).
In a 500 mL round bottom flask, methoxy-4-(prop-2-ynyloxy)benzene (8.88 g, 60.0 mmol), K₂CO₃ (33.1 g, 240 mmol), KI (0.830 g, 5.00 mmol), 1,10-dibromodecane (54.0 g, 180.0 mmol) and acetonitrile (300 mL) were added. The reaction mixture was stirred at reflux for 48 hours. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl₃ (200 mL) and washed twice with H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was recrystallized with CH₃CN to give the intermediate 2b as a white solid (22.6 g, 86 %) as a white solid. The proton NMR spectrum of 2b is shown in Fig. S7. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 6.92 (d, J = 8 Hz, 4H), 6.84 (d, J = 8 Hz, 4H), 4.63 (s, 4H), 3.90 (t, J = 12 Hz, 4H), 2.50 (t, J = 8 Hz, 2H), 1.77–1.73 (m, 4H), 1.45–1.42 (m, 4H), 1.32 (m, 8H). The ¹³C NMR spectrum of 2b is shown in Fig. S8. The ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm): 154.05, 151.56, 116.10, 115.32, 78.96, 75.30, 68.54, 56.62, 29.51, 29.40, 29.37, 26.06.
Copper sulfate pentahydrate \([\text{CuSO}_4 \cdot 5\text{H}_2\text{O}, 0.68 \text{ g}, 2.8 \text{ mmol}]\) was added to a solution of \(2a\) (1.34 g, 10.8 mmol) and \(2b\) (1.89 g, 5.4 mmol) in DMF (30 mL). Sodium ascorbate (1.0 g, 5.4 mmol) was then added and the solution was stirred at 90 °C for 12 h. The reaction mixture was poured into brine (200 mL) and extracted with \(\text{CH}_2\text{Cl}_2\) (2 × 100 mL). The organic layer was dried over anhydrous \(\text{Na}_2\text{SO}_4\) and concentrated under vacuum. The residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate 1 : 10) to afford product 2 (2.9 g, 90 %) as a white solid. The
proton NMR spectrum of 2 is shown in Fig. S9. $^1$H NMR (400 MHz, CDCl$_3$, 298K) $\delta$ (ppm): 7.60 (s, 2H), 6.92 (d, $J$ = 8 Hz, 4H), 8.84 (d, $J$ = 8 Hz, 4H), 5.16 (s, 4H), 4.43 (t, $J$ = 12 Hz, 4H), 3.90 (t, $J$ = 8 Hz, 4H), 2.41 (t, $J$ = 8 Hz, 4H), 2.11–2.08 (m, 4H), 1.77–1.63 (m, 9H), 1.45–1.32 (m, 14H). The $^{13}$C NMR spectrum of 2 is shown in Fig. S10. The $^{13}$C NMR (100 MHz, CDCl$_3$, 298K) $\delta$ (ppm): 153.79, 152.16, 144.89, 122.53, 118.91, 115.81, 115.41, 68.57, 62.73, 49.24, 29.48, 29.36, 29.06, 26.04, 22.32, 16.71.

**Fig. S9** $^1$H NMR spectrum (400 MHz, chloroform-$d$, 298K) of 2.

**Fig. S10** $^{13}$C NMR spectrum (100 MHz, chloroform-$d$, 293K) of 2.
4. Determination of diffusion coefficient $D$

![Graph showing concentration dependence of diffusion coefficient](image)

**Fig. S11** Concentration dependence of diffusion coefficient $D$ (500 MHz, CDCl$_3$, 298K).

As the monomer concentration increased from 11.0 mM to 200 mM in solution, the measured weighted average diffusion coefficient decreased considerably from $3.31 \times 10^{-10}$ m$^2$s$^{-1}$ to $1.86 \times 10^{-11}$ m$^2$s$^{-1}$, indicating the concentration dependence of supramolecular polymerization and the formation of a high weight polymer structure.

5. SEM images of supramolecular polymer after addition of H$_2$O$_2$ and GSH

![SEM images](image)

**Fig. S12** SEM images of (c) the linear supramolecular polymer after addition of H$_2$O$_2$ and (d) the linear supramolecular polymer after addition of GSH.
6. Partial $^1$H NMR spectra of 1 and 2 after using $\gamma$-radiation

**Fig. S13** (a) $^1$H NMR spectra (500 MHz, 298 K) of 1 and 2 in CDCl$_3$ at 88.0 mM. (b) after using $\gamma$-radiation at 50 Gy for 1 hour.

7. Reaction mechanism of diselenide group after adding $H_2O_2$ or GSH

**Fig. S14** Chemdraw structures of reaction mechanism of diselenide group after adding $H_2O_2$ or GSH.
References:

